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岷江金丝桃中一个新的间苯三酚类化合物

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摘要: 从岷江金丝桃 (*Hypericum henryi* subsp. *uraloides*) 中分离得到了一个新的间苯三酚类化合物 (**1**), 命名为 uraloidin A。其结构主要通过 MS, 1D 以及 2D NMR 等波谱方法鉴定。同时, 还得到 7 个已知化合物。

关键词: 岷江金丝桃; 藤黄科; 间苯三酚; uraloidin A
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A New Polyisoprenylated Benzoylphloroglucinol Derivative from *Hypericum henryi* subsp. *uraloides* (Guttiferae)

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Abstract: A new polyisoprenylated benzoylphloroglucinol derivative, uraloidin A (**1**), together with seven known compounds (**2-8**) were isolated from the aerial parts of the *Hypericum henryi* subsp. *uraloides*. Their structures were established on the basis of spectral evidence (MS, IR, 1D- and 2D NMR experiments).

Key words: *Hypericum henryi* subsp. *uraloides*; Guttiferae; Polyisoprenylated benzoylphloroglucinol; uraloidin A

The antidepressant activity of the extract of St. John′s wort (*Hypericum perforatum* L.) extracts has encouraged the investigation of secondary metabolites from *Hypericum* species, many of which are acylphloroglucinol derivatives (Verotta, 1999; Verotta, 2000). *Hypericum henryi* subsp. *uraloides* (Rehd.) N. Robson distributed widely in Yunnan, Sichuan, Guizhou provinces in China, and middle of Burma. Up to now, there is no report on its chemical constituents. For the sake of seeking more novel bioactive compounds, we carried out extensive chemical studies on the aerial parts of *H. henryi* subsp. *uraloides*. In this paper, we described the isolation and structural elucidation of a new polyisoprenylated benzoylphloroglucinol derivative. Seven known compounds were oleanolic acid (**2**) (Maillard *et al.*, 1992), betulinic acid (**3**) (Wenkert *et al.*, 1978), quercetin (**4**) (Wanger *et al.*, 1976), 1, 5, 6-trihydroxy-3-methoxyxanthone (**5**) (Terreaux *et al.*, 1995), 1, 3, 5, 6-tetrahydroxyxanthone (**6**) (Jiang *et al.*, 2003), kielcorin (**7**) (Shoer *et al.*, 1989) and 1, 3, 5, 6-tetrahydroxy-4-prenylxanthone (**8**) (Wu *et al.*, 1998).

Results and Discussion

Compound **1** was isolated as a colorless viscous oil, the molecular formula of **1** was determined to be $C_{38}H_{50}O_5$ by negative-ion HR-ESI-MS at m/z 585.3590 (calcd. 585.3580). The IR spectrum showed hydroxyl and double bond absorption bands at 3441 and 1629 cm^{-1}, respectively. The ^{13}C NMR spectrum (Table 1)

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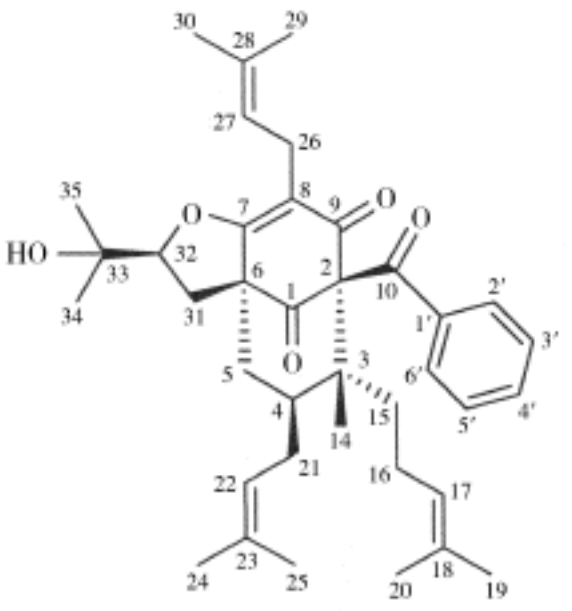
Table 1 NMR Data (acetone-d_6) for **1** (δ in ppm, J in Hz)

No.	δ_H	δC	No.	δ_H	δ_C
1	-	206.2 (s)	22	5.09 (d, 8.4)	123.4 (d)
2	-	80.2 (s)	23	-	133.8 (s)
3	-	50.1 (s)	24	1.68 (s)	26.0 (q)
4	1.90 (m)	43.8 (d)	25	1.61 (s)	18.0 (q)
5	1.79 (m), 2.29 (d, 3.96)	39.4 (t)	26	2.97 (dd, 7.3, 13.9), 3.10 (dd, 7.5, 13.9)	22.8 (t)
6	-	60.9 (s)	27	5.16 (t, 7.4)	122.1 (d)
7	-	174.3 (s)	28	-	132.5 (s)
8	-	116.0 (s)	29	1.62 (s)	25.82 (q)
9	-	193.8 (s)	30	1.61 (s)	17.9 (q)
10	-	194.9 (s)	31	1.97 (dd, 6.0, 13.1), 2.71 (dd, 10.2, 13.0)	30.0 (t)
14	1.17 (s)	14.7 (q)	32	4.80 (dd, 6.0, 10.2)	91.6 (d)
15	1.54 (m), 2.14 (m)	37.3 (t)	33	-	70.7 (s)
16	2.04 (m), 2.22 (m)	25.79 (t)	34	1.35 (s)	26.2 (q)
17	5.06 (d, 7.0)	125.7 (d)	35	1.22 (s)	25.7 (q)
18	-	131.4 (s)	1′	-	138.0 (s)
19	1.64 (s)	25.9 (q)	2′, 6′	7.48 (d, 7.4)	128.9 (d)
20	1.64 (s)	17.8 (q)	3′, 5′	7.25 (t, 7.8)	128.6 (d)
21	1.92 (t, 3.1), 2.26 (m)	27.9 (t)	4′	7.43 (t, 7.4)	132.7 (d)



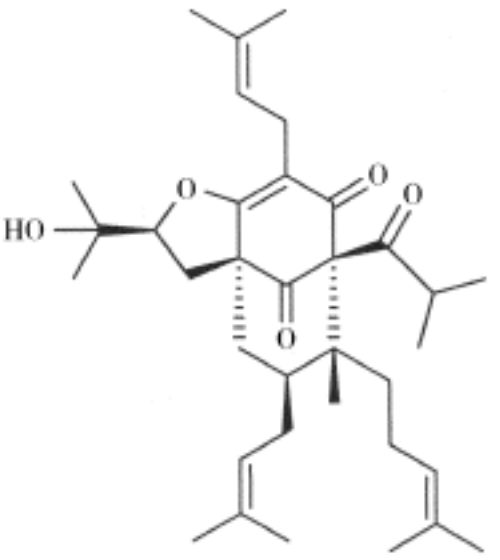


Fig. 1 The structures of **1** and furohyperforin

showed 38 carbon signals including three carbonyl groups (δ_C 206.2, 194.9, 193.8), a benzene ring (δ_C 138.0, 128.6 × 2, 128.9 × 2, 132.7), nine methyls, six methylenes, five methines, one of which bore an oxygen atom (δ_C 91.6), and nine quaternary carbones (including four saturated and one oxygened). In Addition, it is noteworthy that C-7 (δ_C 174.3) was an quaternary carbon of enol connected to the oxygen atom. The ^{1}H NMR spectrum also exhibited the presence of nine singlet methyls, a mono-substituated benzene ring [(δ_H 7.48 (d, J = 7.4 Hz), 7.25 (t, J = 7.8 Hz), 7.43 (t, J = 7.4 Hz)] and three tri-substituted double bonds at 5.06 (d, J = 7.0 Hz), 5.09 (d, J = 8.4 Hz) and 5.16 (t, J = 7.4 Hz). Further analysis of 2D NMR spectra using HSQC and HMBC techniques enabled the assignment of ^{1}H and ^{13}C NMR signals.

The above-mentioned data disclosed that **1** was a polyisoprenyland benzoylphloroglucinol derivative. The ^{13}C NMR of **1** was very similar to those of furohyperforin (Verotta *et al.*, 1999). Correlations between H-15 (δ_H 1.54 and 2.14) and C-2 (δ_C 80.2), C-3 (δ_C 50.1), C-4 (δ_C 43.8) and C-14 (δ_C 14.7), H-21 (δ_H 1.92 and 2.26) and C-4 (δ_C 43.8), C-5 (δ_C 39.4), H-26 (δ_H 2.97, 3.10) and C-7 (δ_C 174.3), C-9 (δ_C 193.8), H-31 (δ_H 1.97 and

2.71) and C-5 (δ_C 39.4), C-6 (δ_C 60.9) in HMBC spectrum (Fig. 2) also confirmed the similarity of **1** and furohyperforin. The only difference between them emerged at C-10, in which the substituent group was a benzene ring in **1**, replaced the isopropyl group in furohyperforin. Correlations between H-2′ and 6′ (δ_H 7.48) and C-10 (δ_C 194.9) in HMBC spectrum suggested that the benzene ring was attached to C-10.

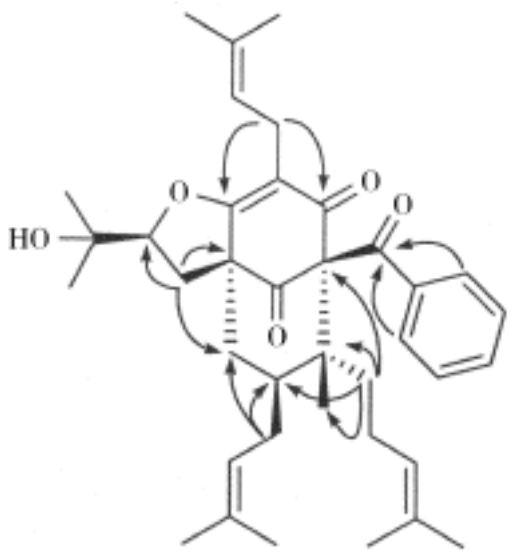


Fig. 2　Key HMBC correlations for **1**

ROESY correlation between H-32 (δ_H 4.80) and H-5a (δ_H 2.29), incombination with biogenetic considerations, indicated that the configuration of **1** was the same as that in furohyperforin. Thus the structure of **1** was assigned as shown in Fig. 1, named uraloidin A.

Experimental

General　Optical rotations were measured on a Horiba SEPA-300 automatic digital polarimeter. IR spectra were conducted on a Bio-Rad FTS-135 spectrometer with KBr pellets. UV spectra were obtained on a UV 2401 PC spectrometer. ^{1}H, ^{13}C NMR and 2D NMR spectra were recorded on a DRX-500 NMR spectrometer with TMS as internal standard. MS data were obtained on a VG Autospec-3000 spectrometer. HPLC separations were performed on a HP 1100 apparatus equipped with a diode array UV detector and ZORBAX SB-C18 (9.4 × 250 mm) column. Column chromatography were performed on silica gel (200-300 mesh, Qingdao Marine Chemical Inc. China), Lichroprep RP-18 gel (40-63 μm, Merck, Dramstadt, Germany) and Sephadex LH-20 (25-100 μm, Amersham Biosciences, Sweden). Thin-layer chromatograph (TLC) was carried out on silica gel 60 F_{254} on glass plates (Merck) using various solvent systems.

Plant material　The aerial parts of *H. henryi* subsp. *uraloides* were collected from Jinpin, Yunnan Province, China in July 2007 and identified by Associate Prof. Yu Shaowen at Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation　The dried and powdered aerial parts of 4.0 kg of *H. henryi* subsp. *uraloides* were extracted with MeOH for three times under room temperature and then concentrated under reduced pressure. The concentrated MeOH extract (810 g) was dissolved in water and extracted with petroleum ether and ethyl acetate step by step, obtained 110 g petroleum ether extract and 45 g ethyl acetate extract. The petroleum ether extract was subjected to silica gel column chromatograph with petroleum ether-AcOEt (1∶0 to 5∶5, then acetone) and obtained fractions 1-7. Each fraction was further purified by repeated CC (silica gel, Rp-18, Sephadex LH-20) then HPLC to give compounds: **1** (16.45 mg), **2** (11.5 mg), **3** (120 mg). The petroleum ether extract was subjected to silica gel column chromatograph with petroleum ether-AcOEt (1∶1 to 4∶6, then acetone) and obtained fractions 1-4. Each fraction was further purified by repeated CC (silica gel and Sephadex LH-20) to afford compounds: **4** (160 mg), **5** (9.72 mg), **6** (81.6 mg), **7** (62.9 mg), **8** (238.6 mg).

uraloidin A (**1**): $C_{38}H_{50}O_5$, colorless oil; $[\alpha]_D^{28}$ -55.0 (*c* 0.10, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 204 (4.6) nm; IR (KBr) ν_{max} 3441, 3074, 2923, 1638, 1629, 1510, 1499, 1449, 1408 cm^{-1}; ^{1}H and ^{13}C NMR data see Table 1; HRES-IMS *m*/*z* 585.3590 (calcd for [M-H]$^-$, 585.3580).

oleanolic (**2**): $C_{30}H_{50}O_3$, white powder; ^{13}C NMR (100 MHz, CD_3Cl): δ_C 38.4 (t, C-1), 26.9 (t, C-2), 78.9 (d, C-3), 39.2 (s, C-4), 55.2 (d, C-5), 18.2 (t, C-6), 32.6 (t, C-7), 38.6 (s, C-8), 47.6 (d, C-9), 37.0 (s, C-10), 22.9 (t, C-11), 122.3 (d, C-12), 143.7 (s, C-13), 41.1 (s, C-14), 27.6 (t, C-15), 23.3 (t, C-16), 46.3 (s, C-17), 41.6 (d, C-18), 45.9 (t, C-19), 30.6 (s, C-20), 33.8 (t, C-21), 32.4 (t, C-22), 28.0 (q, C-23), 15.5 (q, C-24), 15.2 (q, C-25), 16.8 (q, C-26), 25.8 (q, C-27), 181.2 (s, C-28), 33.0 (q, C-29), 23.5 (q, C-30).

betulinic acid (**3**): $C_{30}H_{48}O_3$, white powder; ^{13}C NMR (100 MHz, CD_3Cl): δ_C 38.7 (t, C-1), 27.3 (t, C-2), 78.9 (d, C-3), 38.8 (s, C-4), 55.3 (s, C-5), 18.2 (t, C-6), 34.3 (t, C-7), 40.6 (s, C-8), 50.5 (d, C-9), 37.1 (s, C-10), 20.8 (t, C-11), 25.4 (t, C-12), 38.3 (d, C-13), 42.4 (s, C-14), 29.6 (t, C-15), 32.1 (t, C-16), 56.2 (s, C-17), 49.2 (d, C-18), 46.8 (d, C-19), 150.3 (s, C-20), 30.5 (t, C-21), 37.0 (t, C-22), 27.9 (q, C-23), 15.3 (q, C-24), 16.1 (q, C-25), 16.0 (q, C-26), 14.6 (q, C-27), 179.2 (s, C-28), 109.6 (t, C-29), 19.3 (q, C-30).

quercetin (**4**): $C_{15}H_{10}O_7$, yellow powder; ^{1}H NMR (400 MHz, acetone-d_6): δ_H 6.25 (1H, d, *J* = 1.5 Hz, H-6),

6.51 (1H, d, J = 1.5 Hz, H-8), 7.82 (1H, d, J = 1.7 Hz, H-2′), 6.98 (1H, d, J = 6.8 Hz, H-5′), 7.69 (1H, dd, J = 1.7, 6.8 Hz, H-6′); ^{13}C NMR (100 MHz, acetone-d_6): δ_C 146.9 (s, C-2), 136.7 (s, C-3), 176.5 (s, C-4), 157.7 (s, C-5), 99.1 (d, C-6), 164.9 (s, C-7), 94.4 (d, C-8), 162.3 (s, C-9), 104.1 (s, C-10), 121.4 (s, C-1′), 115.7 (d, C-2′), 145.8 (s, C-3′), 148.3 (s, C-4′), 116.2 (d, C-5′), 123.7 (d, C-6′).

1, 5, 6-trihydroxy-3-methoxyxanthone (**5**): $C_{14}H_{10}O_6$, yellow powder; ^{1}H NMR (400 MHz, DMSO): δ_H 6.34 (1H, d, J = 1.6 Hz, H-2), 6.57 (1H, d, J = 1.6 Hz, H-4), 6.93 (1H, d, J = 7.0 Hz, H-7), 7.50 (1H, d, J = 7.0 Hz, H-8); ^{13}C NMR (100 MHz, DMSO): δ_C 162.6 (s, C-1), 96.7 (d, C-2), 165.9 (s, C-3), 92.6 (d, C-4), 157.2 (s, C-4a), 132.5 (s, C-5), 152.1 (s, C-6), 113.2 (d, C-7), 115.9 (d, C-8), 179.9 (s, C-9), 102.3 (s, C-9a), 146.2 (s, C-10a), 56.0 (q, C-OMe).

1, 3, 5, 6-tetrahydroxyxanthone (**6**): $C_{13}H_8O_6$, yellow powder; ^{1}H NMR (400 MHz, DMSO): δ_H 6.22 (1H, d, J = 1.7 Hz, H-2), 6.41 (1H, d, J = 1.7 Hz, H-4), 6.97 (1H, d, J = 7.0 Hz, H-7), 7.61 (1H, d, J = 7.0 Hz, H-8); ^{13}C NMR (100 MHz, DMSO): δ_C 164.7 (s, C-1), 98.8 (d, C-2), 165.8 (s, C-3), 94.7 (d, C-4), 158.7 (s, C-4a), 133.1 (s, C-5), 152.1 (s, C-6), 113.6 (d, C-7), 117.4 (d, C-8), 181.1 (s, C-9), 103.0 (s, C-9a), 146.8 (s, C-10a).

kielcorin (**7**): $C_{23}H_{18}O_7$, yellow powder; ^{1}H NMR (400 MHz, DMSO): δ_H 7.16 (1H, s, H-1), 7.65 (1H, d, J = 8.4 Hz, H-5), 7.82 (1H, m, H-6), 8.17 (1H, dd, J = 1.5, 7.9 Hz, H-8), 7.06 (1H, d, J = 1.8 Hz, H-2′), 6.83 (1H, d, J = 8.1 Hz, H-5′), 6.90 (1H, dd, J = 1.8, 8.2 Hz, H-6′), 5.06 (1H, d, J = 7.9 Hz, H-7′), 4.38 (1H, m, H-8′), 3.44 (1H, m, H-9′a), 3.71 (1H, m, H-9′b), 3.78 (3H, s, OMe), 3.84 (3H, s, OMe); ^{13}C NMR (100 MHz, DMSO): δ_C 96.6 (d, C-1), 147.4 (s, C-2), 139.6 (s, C-3), 132.5 (s, C-4), 155.3 (s, C-4a), 141.2 (s, C-10a), 118.0 (d, C-5), 134.7 (d, C-6), 124.2 (d, C-7), 125.8 (d, C-8), 113.9 (s, C-8a), 174.7 (s, C-9), 105.8 (s, C-9a), 126.6 (s, C-1′), 112.2 (d, C-2′), 145.8 (s, C-3′), 147.7 (s, C-4′), 115.5 (d, C-5′), 134.7 (d, C-6′), 76.3 (d, C-7′), 77.8 (d, C-8′), 59.9 (t, C-9′).

1, 3, 5, 6-tetrahydroxy-4-prenylxanthone (**8**): $C_{18}H_{16}O_6$, yellow powder; ^{1}H NMR (400 MHz, DMSO): δ_H 6.48 (1H, s, H-2), 6.89 (1H, d, J = 8.7 Hz, H-7), 7.48 (1H, d, J = 8.7 Hz, H-8), 3.21 (2H, d, J = 6.8 Hz, H-1′), 5.17 (1H, t, J = 6.4 Hz, H-2′), 1.71, 1.61 (each 3H, 3′-Me); ^{13}C NMR (100 MHz, DMSO): δ_C 93.3 (d, C-2), 159.8 (s, C-3), 109.7 (s, C-4), 155.1 (s, C-4a), 132.4 (s, C-5), 151.8 (s, C-6), 113.0 (d, C-7), 115.9 (d, C-8), 112.9 (s, C-8a), 179.7 (s, C-9), 101.2 (s, C-9a), 146.0 (s, C-10), 21.0 (t, C-1′), 122.4 (d, C-2′), 130.6 (s, C-3′), 17.7 (q, C-4′), 25.5 (q, C-5′).

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References:

Jiang DJ, Hu GY, Jiang JL *et al.*, 2003. Relationship between protective effect of xanthone on endothelial cells and endogenous nitric oxide synthase inhibitors [J]. *Bioorg Med Chem*, **11**: 5171—5177

Maillard M, Adewunmi CO, Hostettmann KH, 1992. A triterpene glycoside from the fruits of *Tetrapleura tetraptera* [J]. *Phytochemistry*, **31**: 1321—1323

Shoer MA, Habib AA, Chang CJ *et al.*, 1989. Seven xanthonolignoids from *Psorospermum febrifugum* [J]. *Phytochemistry*, **28**: 2483—2487

Terreaux C, Maillard M, Gupta MP *et al.*, 1995. Xanthones from *Schultesia lisianthoides* [J]. *Phytochemistry*, **40**: 1791—1795

Verotta L, Appendina G, Belloro E *et al.*, 1999. Furohyperforin, a prenylated phloroglucinol from St. John's Wort (*Hypericum perforatum*) [J]. *J Nat Prod*, **62**: 770—772

Verotta L, Appendina G, Jakupovic J *et al.*, 2000. Hyperforin analogues from St. John's Wort (*Hypericum perforatum*) [J]. *J Nat Prod*, **63**: 412—415

Wanger H, Chari VM, Sonnenbichler J, 1978. ^{13}C-NMR-Spektren natürlich vorkommender flavonoide [J]. *Tetrahedron Lett*, **17**: 1799—1802

Wenkert E, Baddeley V, Burfitt IR *et al.*, 1987. Carbon-13 nuclear magnetic resonance spectroscopy of naturally-occurring substances [J]. *Org Magnetic Res*, **11**: 337—342

Wu QL, Wang SP, Du LJ *et al.*, 1998. Xanthones from *Hypericum japonicum* and *H. henryi* [J]. *Phytochemistry*, **49**: 1395—1402